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Separation of antimony and tin in alloy

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SEPARATION OF ANTIMONY AND TIN IN ALLOY

BY

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THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMICAL ENGINEERING

IN THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Lawrence Charles Turnock

ENTITLED Separation of Antimony and Tin in Alloys

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

In Chemical Engineering

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A rapid and accurate method for the separation and determination of antimony and tin has at the present time a wide field for application owing to the fact that the use of these two metals in the many different alloys of to-day is very extensive. Possibly the most important alloys which contain tin and antimony alloyed together with other metals are the different brasses and bearing metals, the latter often commonly known as Babbitts, though a true Babbitt alloy is composed of zinc, tin, and copper. An early type of bearing metal consisted of two parts of antimony, six parts of tin, and one part of copper, but at the present time these vary within quite wide limits, and in addition to them different proportions of lead, iron, and zinc are now added in order to give the alloy certain desired physical properties not otherwise acquired by the presence of the first three elements alone. Another common alloy of tin and antimony is Britannia metal, containing about 90.5% tin, 8.0% antimony, and 1.5% copper.

Antimony and tin do not always occur together in different alloys. There are a great many alloys which contain antimony alone, or tin alone, mixed together with one or more other metals in varying proportions. For example, tin, copper, and zinc are alloyed to form the bronzes, gun metals, and bell metals, and, furthermore, type metal is an alloy of antimony and lead. Here, then, the problem does not lie in the separation of antimony and tin from each other, but in the separation of either antimony or tin from the other metals in the alloy, and in finding a rapid as well as an accurate and satisfactory method for determining the proportions in which the antimony exist in the alloy.

The reason for mixing the different metals together in

varying proportions as well as in numbers is that by so doing a resulting alloy is obtained, whose desired physical properties are those designed to meet a specific purpose. The alloying of metals at the present time has not by any means reached its maximum point of perfection, but, on the otherhand, we know through experience what properties different metals themselves have and also what properties they give by adding them in different amounts to certain other metals or mixtures of metals. Some increase the hardness, others brittleness, some ductility, and others specific gravity, until we have at present alloys containing not only two or three but as high as seven or eight metals. Antimony usually imparts to its alloys a hardness and brittleness and also increases its fusibility. Another matter which is of vast practical importance is the substitution of cheaper metals in an alloy in place of the more expensive ones, and which at the same time will not destroy any of the desired physical properties of the alloy. For instance, by lowering the percentage of tin in an alloy and substituting copper and lead in its place, the alloy retains the same properties it had with the exception of hardness, and this is furnished by the addition of antimony.

We have learned through experience that alloys of certain definite composition are best adapted to a specific use, and that an any slight varation any way in the percentage of the metal in the alloy will very often materially affect its physical properties. It has, therefore, become necessary that we have a method for accurately and quickly determining the exact ratio in which the different metals compose the alloy. Since antimony and tin often exist together in many alloys their separation is one of importance. Among

the many proposed methods for their separation, the following may be mentioned.

A method known as Garnot's² consists in the treatment of a neutral HCl solution of tin and antimony which with an excess of oxalic acid, which prevents the precipitation of the tin upon adding a solution of sodium thiosulphate. If the oxalic acid is not in considerable excess, tin will precipitate and in fact does anyway, wherein lies the difficulty. The precipitation of the antimony, on the otherhand, is very complete, but owing to the fact that some tin is mixed in occasionally, the results vary.

Drown's³ method consists in the separation of arsenic, antimony, and tin from one another and depends upon the volatilization of the chloride of tin, arsenic, and antimony and their absorption in a solution of potassium bromide, from which the arsenic is distilled and the antimony and tin separated according to Garnot's method.

In Kassner's⁴ method the sulphides of tin, arsenic, and antimony are treated with sodium peroxide which dissolves them and partially reprecipitates the tin. Long continued boiling will precipitate the tin as oxide, and the antimony is determined in the filtrate by adding alcohol which causes a separating out of pyroantimonic acid. In testing out this method, I was unable to obtain a complete precipitation of the pyroantimonic acid, though a complete precipitation of the tin is possible by long boiling.

Bunsen⁵ suggests a method for the separation of antimony

² Zeit. fur Anal. Chemie - Vol. 27 - p. 651.

³ Zeit. fur Anal. Chemie - Vol. 39 - p. 47.

⁴ Zeit. fur Anal. Chemie - Vol. 34 - p. 596.

⁵ Analen der Chemie - Vol. 192 - p. 317.

and arsenic by first precipitating the metals as sulphides and then redissolving them in a five percent solution of KOH. The arsenic is now separated by volatilizing in a stream of chlorine gas. The main difficulty in this method lies in the fact that it does not take account of the difficulty of dissolving antimonic sulphide in KOH, and also that it is almost impossible to effect a complete volatilization and collection of the contents. The criticism to which this method may be subjected is that it does not account for the handling of any tin and also that any method involving the volatilization of some one of the products is to be avoided, if possible, in technical work.

In Warren's² method the antimony and tin are precipitated along with the other sulphides of the second group and separated from them by dissolving out with a solution of KOH. To the filtrate HCl is added causing a reprecipitating of the sulphides, which are filtered and dissolved in aqua regia. The tin is now precipitated as stannic ferrocyanide by adding a solution of $K_4Fe Cy$, while the antimony remains in solution, antimonic ferrocyanide being unknown. The objection to this method lies in the fact that if a solution of KOH much over 2% or 3% in strength is used and added in too large quantities, the tin will reprecipitate. These conditions must be regulated before the method is reliable.

Dr. A. Weller's³ method for the determination of antimony in the presence of tin is based upon the fact that if a HCl solution

²Chem. News Vol. 57 - p. 125.

³Chem. News Vol. 46 - p. 172.

of $SbCl_5$ and $SnCl_4$ is treated with HI , the $SbCl_5$ is reduced to $SbCl_3$, liberating an equivalent amount of iodine, while the $SnCl_4$ remains in the stannic form. The liberated iodine is distilled over into a KI solution and titrated when cold with H_2SO_3 . The main objection to this method is that as a rule distillation methods are not received with favor by industrial chemists.

In a method proposed by Carson, Lange, and Mackintosh² the sulphides of tin, arsenic, and antimony are treated with concentrated HNO_3 and brought to dryness. By extracting the residue with water the arsenic is dissolved and determined by precipitating with a magnesia mixture. The remaining residue is now digested with tartaric acid, which extracts the antimony and leaves the tin as tin oxide.

In a method worked out by McKay³ for the separation of antimony and tin, the antimony is completely precipitated as Sb_2S_3 when H_2S is passed into a HFl solution containing large amounts of sodium acetate, and in which the antimony exists in the antimonous state and the tin in the stannic state. The tin under these conditions remains in solution. Since in the regular course of analysis, antimony and tin are obtained in the form of sulphides, and since these sulphides are soluble in concentrated HCl with the formation of antimonous and stannic chlorides, no difficulty is encountered in obtaining a solution containing the antimony in the lower and the tin in the upper state of oxidation. The criticism open to this method is the use of so much HFl , which besides being objectionable in the laboratory requires the use of so much platinum

² School of Mines Quarterly Vol. 24 - p. 90.
³ Jour. Am. Chem. Soc. May, 1909.

or paraffin-coated glass.

Dinam's² method for the separation of arsenic, antimony, and tin and its application to the analysis of bronze consists in the treating the bronze with nitric acid, which puts into solution all the lead, copper, and zinc and leaves the tin, antimony, and arsenic in the residue. The residue is now dissolved by adding a considerable amount of oxalic acid and ammonium oxalate and a little HCl, diluted, precipitated with H_2S , and the tin determined by electrolysis in the filtrate. The sulphides of arsenic and antimony are now dissolved in KOH, a definite amount of HCl added, and the solution boiled to expel the H_2S . The arsenic is precipitated as the sulphide, while the antimony remains in solution. The filtrate is oxidized with HCl and $KClO_3$, treated with KI, boiled to expel the Cl, and the liberated iodine titrated with $Na_2S_2O_3$. The As_2S_3 is dissolved in KOH, oxidized with HCl and $KClO_3$, boiled to expel the chlorine, treated with KI, and the free iodine titrated with $Na_2S_2O_3$.

In a method proposed by M. A. Berg³ for the separation of antimony and tin with reference to its presence in alloys, the alloy in a finely divided state is mixed with equal parts of sodium carbonate and sulphur, heated in a porcelain crucible, cooled, and treated with water. The tin is transformed to Na_2SnS_3 which is soluble in H_2O , while the antimony changes to Sb_2S_3 , which, on the otherhand, is insoluble in water.

G. Panajotow's⁴ method for the separation of antimony and

²Mon.Sci. - 22, 600 - 602.

³Bull. Soc. Chin. Vol.4, p. 905.

⁴Ber. Vol. 42 - p.1296.

tin is based on the fact that if H_2S is passed into a solution containing both the antimony and tin with 15% of HCl and cooled to below 30 degrees C, the antimony is precipitated while the tin remains in solution.

The above is a fairly complete outline of the methods now in use for the separation of antimony and tin. They may be divided into four different classes, viz, first, those in which yellow ammonium sulphide is used to separate the sulphides of arsenic, antimony, and tin from the other sulphides of the second group; second, those in which alkali KOH is used to dissolve out the tin, antimony, and arsenic sulphides from the other sulphides precipitated in the second group; third, those in which the tin, antimony, and arsenic are separated from the lead, copper, zinc, and iron by dissolving the alloy in HNO_3 which leaves only the tin, antimony, and arsenic in the residue; and fourth, by fusing the finely divided alloy with sodium carbonate and sulphur. Objections, however, may be found with all of them, and especially with those in which the yellow ammonium sulphide is used. In the method where As, Sn, and Sb are separated from the Pb, Cu, Fe, and Zn by treating the alloy with HNO_3 , you are very liable to lose some parts of them by their going into solution along with the Cu, Pb, Fe, and Zn. In the fusion method there is danger of carrying the process on too long, when the antimony will go over into a compound, which is likewise soluble in water, as in the case of tin. The method of separating the sulphides of arsenic, antimony, and tin from the other sulphides of the second group by dissolving out the former in alkalies seems to be best and cleanest. In this work it was decided to study the

effect of alkalis on the sulphides of the second group and to devise a means, if possible, of separating the antimony and tin from each other after they were separated from the sulphides of the second group. There are some methods, which although they may give results as accurate as could be wished for, still are not received with much favor by industrial chemists. What is wanted in a technical laboratory are methods that are not only accurate and inexpensive, but rapid, and at the same time requiring a minimum amount of manipulation.

EXPERIMENTAL WORK

In many of the usual methods yellow ammonium sulphide is used to separate the sulphides of tin, arsenic, and antimony from the other sulphides of the second group. It is well known that all the methods involving the use of this reagent are not only tedious, but also very annoying, owing to the fact that quantities of sulphur will always separate out. Furthermore, they are unreliable and inaccurate because the yellow ammonium sulphide must be in contact with the precipitate for hours before effecting a complete solution of the tin, arsenic, and antimony sulphides, and because the sulphides of bismuth and copper are slightly soluble in this reagent, the latter to the extent of 5.71%². Our attention is, consequently, drawn toward finding a substitute, which at the same time will eliminate the difficulties encountered with in the use of this yellow ammonium sulphide.

² Analyst - Vol. 27, p. 99.

The solubilities of the sulphides of arsenic, antimony, and tin in alkalies has long been known. In methods, however, where the dissolving power of caustic alkalies was made use of, no uniform results could be obtained, because the conditions involving the effect of different strengths and amounts of the alkali upon the sulphides had never been very well studied.

Having decided upon the use of KOH in this work, the first question to be investigated was the solvent action of different strengths of solution upon all the sulphides of the second group. For this purpose a 1/2%, 1%, 1 1/2%, 2%, 3%, and 5% solution of the purest KOH obtainable, was made up, as well as solutions of soluble salts of copper, bismuth, cadmium, mercury, both trivalent and pentavalent antimony and arsenic, and stannous and stannic tin. Hydrogen sulphide was then passed through solutions of the different salts, the precipitate filtered off, washed, and treated with the different strength solutions of KOH. The amount of precipitate in each case amounted to about 0.2 gram and was boiled with 25 cc (added all at once) of the different caustic potash solutions. The following results were observed:

PbS + 1%KOH + boiling = no trace of PbS dissolved.

PbS + 2%KOH + " = " " " " "

PbS + 3%KOH + " = " " " " "

PbS + 5%KOH + " = " " " " "

CuS + 5%KOH + " = " " " " "

Bi₂S₃ + 5%KOH + boiling = no trace of Bi₂S₃ dissolved.

CdS + 5%KOH + boiling = no trace of CdS dissolved.

HgS + 5%KOH + boiling = no trace of HgS dissolved.

As₂S₃ + any strength KOH = complete solution of As₂S₃.

Sb₂S₃ + " " " = " " " Sb₂S₃.

As₂S₅ + 3% or 5%KOH = solution of As₂S₅ with difficulty.

Sb₂S₅ + " " " = " " " Sb₂S₅ " "

SnS + 2%KOH = quantity of SnS dissolved (but not complete solution).

SnS + 5%KOH = " " " " " " " " "

SnS₂ + 1/2%KOH = solution of SnS₂ but partial reprecipitation of Sn.

SnS₂ + 1%KOH = " " " " " " " " "

SnS₂ + 1 1/2KOH = " " " " " " " " "

SnS₂ + 2%KOH = " " " " " " " " "

SnS₂ + 3%KOH = " " " " " " " " "

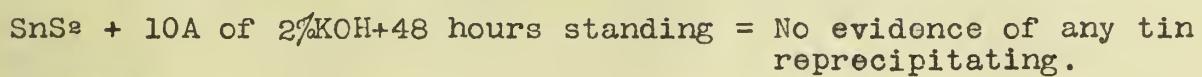
SnS₂ + 5%KOH = " " " " " " " " "

In all the last six cases where SnS_2 was treated with KOH, the sulphide easily dissolved in the cold, but the tin was reprecipitated on standing. Furthermore, its precipitation was accelerated upon heating and boiling, and the larger the excess of KOH present and the stronger the solution of the caustic potash, the more rapid did seem the precipitation. Tests were now made to ascertain what effect the strength and amount of KOH present had upon the reprecipitation of the tin. About 0.2 grams of freshly precipitated SnS_2 was placed in a beaker and KOH slowly and cautiously added from a burette until the reaction was just alkaline. The solution was now boiled vigorously and it was observed whether the tin reprecipitated. If not, twice as much KOH as was necessary to react alkaline was added and the solution again boiled and examined for any precipitation of tin. If still no tin reprecipitated, in like manner, three, four, and five times as much KOH was added separately from the burette and the solution boiled and examined after each addition. The following table shows the observed results, "A" denoting the amount of KOH added to dissolve the SnS_2 just necessary to make the solution react alkaline:

Strength of KOH Amount added Reprecipitation of tin.

1/2%	A = 25 cc		None
	2A		"
	3A		"
	4A		"
	5A		"
1%	A = 11.5 cc		"
	2A		"
	3A		"
	4A		"
	5A		"
1 1/2%	A		"
	2A		"
	3A		"
	4A		"
	5A		"
2%	A = 6 cc		"
	2A		"
	3A		"
	4A		"
	5A		"
3%	A		"
	2A		"
	3A		"
	4A		"
	5A		"
5%	A		"
	2A		"
	3A		"
	4A		"
	5A		"

It was also observed that the amount of time the solution of SnS_2 in KOH was allowed to stand was not a factor in causing the tin to reprecipitate, for about 0.2 grams of



Likewise,



The results of these observations tend to show that while SnS_2 is easily dissolved in any strength of KOH , still a reprecipitation of tin only seems to occur when there is too large an excess of the alkali in contact with the precipitate of SnS_2 at a particular instant. In this work a 2%KOH solution was employed and the amount added to effect a solution of the SnS_2 was between three and four times that just necessary to make the solution react alkaline.

When antimony is precipitated with H_2S from pentavalent salts of antimony, both Sb_2S_3 , Sb_2S_5 , and sulphur are formed, due to the reducing action of the H_2S . Consequently, upon treating with KOH , the precipitate goes into solution with difficulty, owing to the fact that sulphur is not readily soluble in KOH , and especially not in weak solutions. On the otherhand, however, from tests above tabulated, Sb_2S_3 dissolves very readily and easily in all strengths of KOH . Furthermore, as SnS is almost insoluble in KOH , and SnS_2 is readily soluble, it is evidently necessary that the tin be in the stannic form.

Since, now, the best results in using KOH to dissolve the sulphides of antimony and tin as they are precipitated along with the other sulphides of the second group metals in the ordinary course of an analysis are obtained when the tin is in the stannic

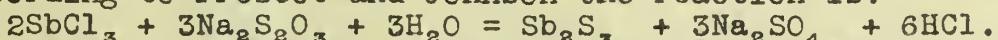
form and the antimony in the antimonous form, it is necessary to employ a satisfactory method by which the antimony can be put into the trivalent state and the tin into the stannic state, before the sulphides of the second group metals are precipitated. First, as it is known that ~~water~~^{H₂O} has an oxidizing effect upon some metals and a reducing effect upon others, it was tried with the result that the stannous tin was in all cases completely and readily oxidized to stannic tin, but, on the otherhand, I could in no way obtain a complete reduction of pentavalent antimony to the trivalent form. Secondly, since it is known that HI, or KI in a strong HCl solution, completely and readily reduces pentavalent antimony to the antimonous state², and at the same time does not reduce stannic to stannous tin, its effect upon an HCl and tartaric acid solution of SbCl₅ and SnCl₄ was observed. The liberated iodine was neutralized by slowly adding a solution of Na₂S₂O₃ or H₂SO₃, the solution diluted, and H₂S passed through. The precipitate was filtered off, washed, and treated with 2% KOH, in which it readily and completely dissolved. In some cases, however, a slight residue remained and dissolved only with the addition of an excess of KOH, and then with some difficulty. This residue proved to be sulphur, which had been precipitated due to an excess of Na₂S₂O₃ or H₂SO₃ being present. By adding the Na₂S₂O₃ cautiously from a burette, or by boiling the solution after the H₂SO₃ is added, this difficulty may be removed and the combined precipitates of antimony and tin will completely and readily dissolve in the KOH.

²Chem. News - Vol. 46, p. 172.

Upon adding an excess of $\text{Na}_2\text{S}_2\text{O}_3$ to the solution to neutralize the iodine which was formed upon reducing pentavalent antimony to trivalent antimony, and boiling the solution, a dark red granular precipitate of antimony came down². This principle is made use of in Garnot's method³ but I could at no time or in any way ever obtain a complete precipitation of the antimony by this method.

Since it was now observed that the best results for completely dissolving out the antimony and tin sulphides from the other sulphides of the second group with KOH could be most satisfactorily accomplished when the antimony existed as trivalent antimony and the tin as stannic tin, it was now necessary to find some means of separating the tin and antimony in the KOH solution from one another. If a solution of Sb_2S_3 , and SnS_2 in KOH is boiled with H_2O_2 , the antimony and tin are completely oxidized to potassium antimonate and stannate. Upon first adding the H_2O_2 the solution turns dark yellow, and then to a lighter yellow upon boiling more. As an indication for serving to ascertain when enough H_2O_2 has been added a fair index is afforded when the solution no longer turns a yellowish color upon adding H_2O_2 . It is perfectly colorless when fully oxidized. If, now, an excess of H_2O_2 is added, the tin will begin to reprecipitate as $\text{Sn}(\text{OH})_4$ and the antimony as pyroantimonic acid. It was now necessary to find some conditions whereby the tin can be completely precipitated and, at the same time, the antimony

² According to Prescott and Johnson the reaction is:



According to Treadwell and Hall's Analytical Chemistry Vol. I, p. 204.
 $2\text{SbCl}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 = 6\text{NaCl} + 4\text{SO}_2 + \text{Sb}_2\text{S}_3\text{O}_6$ oxysulphide.

³ Zeit. fur Anal. Chemie. Vol. 27 - p. 61.

remain in solution. For this purpose qualitative tests with different reagents were run on solutions of SnS_2 and Sb_2S_3 separately dissolved in KOH. These solutions were first carefully oxidized with H_2O_2 , avoiding an excess so that no tin or antimony would reprecipitate, and then divided into aliquot parts upon which tests were run with the following results:

Sb solution + HCl + boiling = precipitate of Sb not complete.

Sb solution + acetic acid + boiling = " " " " "

Sb solution + NH_4Ac + acetic acid = No precipitate of Sb.

Sb solution + KSO_4 = Precipitate of Sb, but not complete, as some dissolved on adding an excess of KOH.

Sn solution + HCl dilute = Partial ppt of tin on dilution.

Sn solution + strong HCl = No precipitate of Sn.

Sn solution + Ac acid + boiling = Complete ppt of Sn on dilution.

Sn solution + NH_4Ac + boiling = " " " " "

Sn solution + KSO_4 + " = " " " " "

Since tin is completely precipitated as $\text{Sn}(\text{OH})_4$ from an alkaline solution of potassium stannate in the presence of acetic acid and ammonium acetate, and antimony, on the otherhand, is not precipitated at all from an alkaline solution of potassium antimonate in the presence of acetic acid and ammonium acetate, these qualitative results suggest a possible method for quantitatively separating tin from antimony.

In order to test it out, a standard tin and antimony solution were made up. Exactly 6.0073 grams of Kalhbaum's best and purest tin were weighed out and dissolved in concentrated HCl with the addition of a little KClO_3 . After all the tin was in solution

and the chlorine expelled by warming on the water bath, 20 grams of tartaric acid were added and the whole made up to one liter. Three portions of 25 cc were taken for analysis and standarized as follows: The solution of 25 cc was treated with a little bromine to make sure that all the tin was in the stannic form and the excess of bromine was expelled. A few cc of HCl were added, the whole diluted to 300 cc, and a rapid stream of H₂S passed through for about 15 minutes. The precipitate was allowed to settle, filtered, washed with hot water, and transferred to the orginal beaker. Two percent KOH was slowly run in from a burette until all the precipitate was in solution, and at the same time the solution was kept warm. It was now oxidized with H₂O₂ and as soon as an excess was present, the tin began to precipitate. About 5 to 10 grams of potassium persulphate were now separately dissolved in water and slowly added to the tin solution, which had been previously diluted to 300 cc and brought up to the boiling point. The tin is immediately precipitated; a few cc of acetic acid will accelerate the precipitation by bringing the solution up to the neutral point. The precipitate is allowed to settle, filtered off, and washed with hot H₂O containing a little NH₄NO₃. It is now dried at 110 degrees to 125 degrees C and ignited to constant weight in a porcelain crucible. The following results were obtained:

<u>Tin taken.</u>	<u>Tin found.</u>
0.1502 grams	0.1503 grams.
0.1502 "	0.1507 "
0.1502 "	<u>0.1501</u> "
Average	0.1503 "

Since it was found in standardizing the tin solution above that the tin could be quantitatively precipitated, a qualitative test on the standard antimony solution was run to see if the antimony would remain in ^{solution} under the same conditions. Twenty-five cc of the antimony solution were taken, diluted to 50 cc, added 10 cc of a 20% solution of potassium iodide and 5 cc of concentrated HCl. This reduced all the pentavalent antimony to the trivalent form. The solution was warmed slightly on the water bath and the iodine neutralized by slowly adding a solution of $\text{Na}_2\text{S}_2\text{O}_3$, a drop at a time. An excess of $\text{Na}_2\text{S}_2\text{O}_3$ is to be avoided as it causes a precipitation of sulphur which is objectionable. The solution is now diluted to 300 cc, warmed, and a rapid stream of H_2S passed thru' for five minutes, in which time all the antimony will precipitate. The precipitate was now filtered off, washed, and transferred to the orginal beaker, dissolved in 60 cc of 2% KOH, diluted to 200 cc, and heated to boiling. Twenty cc of hydrogen peroxide was now added to oxidize the antimony to potassium antimonate, after which I added 30 cc of a ten percent solution of ammonium acetate. To this solution were added 5 grams of KSO_4 previously dissolved in H_2O , and the whole was boiled for 25 minutes without the slightest perceptible precipitate of antimony.

Since, now, under certain conditions it was found that tin could be quantitatively precipitated from a solution of tin, and under the same conditions antimony could not be precipitated from a solution containing antimony, it was next tried to see if tin could be quantitatively separated from antimony in the same solution under the same conditions. For this purpose, 25 cc of the standard tin solution and 25 cc of the standard antimony solution

were mixed together. To make sure that all the tin existed in the stannic form, I added a few drops of bromine, and expelled the excess by warming on a water bath. To this solution I added 10 cc of a 20% potassium iodide solution and 5 cc of concentrated HCl to reduce the antimony to the trivalent state. The liberated iodine was carefully neutralized with $\text{Na}_2\text{S}_2\text{O}_3$. This was best accomplished by adding the $\text{Na}_2\text{S}_2\text{O}_3$ from a burette or pipette, a drop at a time. The whole solution is now diluted to 300 cc, warmed, and a rapid stream of H_2S passed through for 15 minutes. The precipitate is allowed to settle, filtered, washed with hot water containing a little acetic acid and ammonium acetate, transferred to the original beaker and dissolved in 24 cc of 2% KOH, 8 cc of which was enough to make the solution react alkaline. I now heated the solution, added 25 cc of commercial 3% H_2O_2 , when the whole immediately turned reddish and then white with the formation of a voluminous white precipitate. The cause of this precipitation at this point was possibly due to the acid in the H_2O_2 used. The acid reprecipitated the antimony as Sb_2S_3 , which was then immediately oxidized to pyro-antimonic acid by the H_2O_2 .

Three new solutions of 25 cc each of both the standard antimony and tin solutions were prepared, and treated in the same manner as above up to the adding of the hydrogen peroxide. Here, in place of the above 3% solution, the best 30% hydrogen peroxide free from acid that could be obtained was employed. The same reddish color, however, appeared upon adding the 30% H_2O_2 , both the antimony and the tin coming down as a white precipitate. The precipitation of the antimony and tin was complete as the filtrates gave no test for either. Although the 30% H_2O_2 was neutral in

itself, the reprecipitation of Sb_2S_3 as was evidenced by this reddish color was, nevertheless, due to the presence of an acid. This acid may have been sulphuric formed by the oxidation of the sulphur with the hydrogen peroxide. This difficulty of the Sb_2S_3 reprecipitating, then, seemed to be due to the fact that the solution becomes acid before the hydrogen peroxide can oxidize the tin and antimony to potassium stannate and antimonate. Believing this to be the reason, I decided to use more KOH in dissolving the sulphides of antimony and tin.

Three fresh mixtures of 25 c.c. each of the standard tin and antimony solutions were prepared and treated exactly the same as above up to the dissolving of the sulphides. Here, ten times the amount of KOH just necessary to make the solution react alkaline was added, amounting to about 80 c.c. The solutions were now oxidized with 30% H_2O_2 , but in this case no reddish color appeared. Thirty c.c. of 10% ammonium acetate solution were added to keep the antimony up, the whole diluted to 300 c.c., heated to boiling, and 5 grams of potassium persulphate added to it. The precipitate comes down nicely upon boiling and bringing the solution up to the neutral point by adding a few drops of acetic acid. The precipitate was allowed to settle, filtered, washed with hot water containing a little ammonium nitrate, dried, and ignited to constant weight. The following results were obtained:

<u>Weight of SnO_2 taken.</u>	<u>Weight of SnO_2 ppt found.</u>
0.1910 grams	0.2261 grams.
0.1910 "	0.3145 "
0.1910 "	0.2864 "

The results show that the precipitates weighed as SnO_3 are not SnO_2 alone, since the weights are too high. The final weighed precipitate also had a decided grayish metallic appearance, suggesting that antimony was precipitated along with the tin.

It was observed during my qualitative work that under certain conditions antimony would precipitate as pyro-antimonic acid from a solution containing potassium antimonate upon adding a solution of potassium persulphate and boiling, and would also sometimes redissolve upon adding a large excess of KSO_4 . Believing that the KSO_4 was instrumental in precipitating some antimony along with the tin and thus causing the final weighed precipitates to be high, I prepared fresh mixtures of 25 c.c. each of the standard tin and standard antimony solutions and ran the analysis through observing the same precautions as outlined above with the exception that no potassium persulphate was added. This time I obtained the following results:

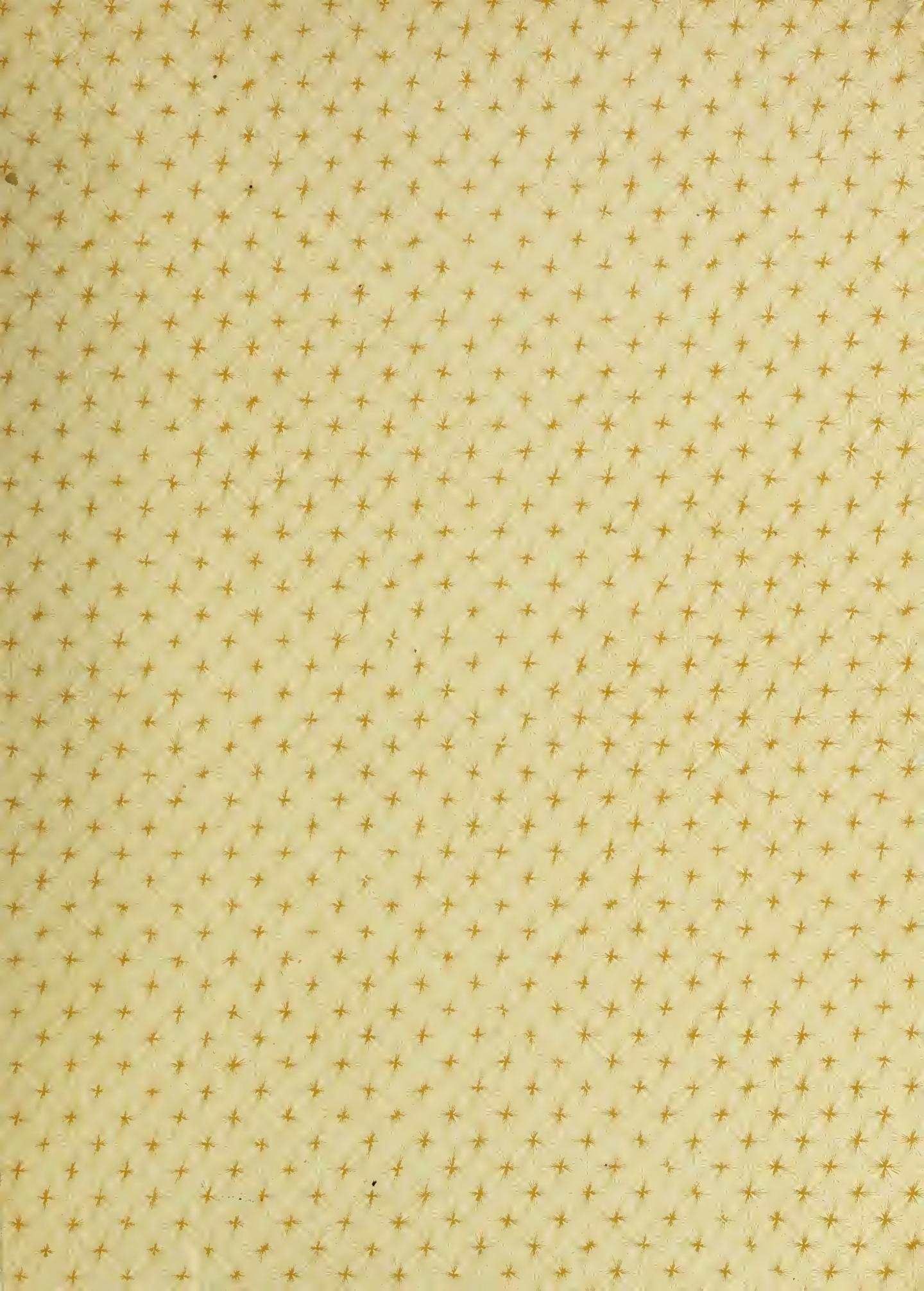
<u>Weight of SnO_2 taken.</u>	<u>Weight of SnO_3 precipitate weighed as SnO_2.</u>
0.1910 grams.	0.2231 grams.
0.1910 "	0.2241 "
0.1910 "	0.2236 "

Although the weights of the precipitates indicate that antimony was precipitated along with the tin, still the amount carried down each time seems to be somewhat constant.

At this point a lack of time prevented carrying on the investigation any further. It was intended here to see if ammonium chloride would act differently than ammonium acetate, and also, instead of directly adding a solution of ammonium acetate to the

solution of potassium antimonate and stannate, to observe the effect of first adding a certain amount of ammonia and then gradually neutralizing with acetic acid. Although the results obtained do not show a complete separation of tin from antimony, nevertheless, since tin can be completely precipitated from a solution of tin under certain conditions, and, on the otherhand, under exactly the same conditions, antimony will not precipitate from a solution containing antimony alone, I feel that if certain other conditions are found, the method may be ^{so}_{modified} as to effect an exact separation of tin from antimony.





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